14190

DEVELOPMENT OF BIO-KINETIC MODEL FOR LUBRICANTS

Dr. In-Sik Rhee, U.S. Army Tank-Automotive Research, Development and Engineering Center

Presented at 2004 NLGI Annual Meeting

BACKGROUND

Biodegradation is a natural process caused by the action of microorganisms, in the presence of oxygen, nitrogen, phosphorous, and trace minerals. Organic pollutants can support microbial growth and are converted into a series of oxidation products that generally conclude with carbon dioxide and water. Modern lubricants are formulated with petroleum based oils or ester oils derived from renewable resources, or chemical synthetic sources. Their biodegradation process is somewhat similar to the fermentation process wherein hydrocarbons are converted into carbon dioxide by the action of metabolism of microorganisms. This biodegradation technology is currently used to remove hazardous materials contaminated in soil, sludge and ground water. Wastewater treatment process is one of its application areas[1, 2].

Recently, the ASTM D-2 Subcommittee 12 on Environmental Standard of Lubricants has developed the ASTM D 5864, Standard Test Method for Determining Aerobic Biodegradation of Lubricants and Their Components. This test method is a version of the Organization for Economic Co-Operation and Development (OECD) Sturn test that closely simulates the wastewater biodegradation conditions and was designed to determine the degree of aerobic aquatic biodegradation of lubricants on exposure to an inoculum under laboratory conditions[3, 4]. In this test, the biodegradability of a lubricant is expressed as the percentage of maximum carbon conversion under well –controlled conditions for a period of 28 days. This test method has been widely used to determine the biodegradability of lubricants in the laboratory. The advantages of this test method are to provide a meaningful data and its low cost of the test apparatus. But the test method requires a long testing time, the knowledge of microorganisms, and manpower. In addition, it has very poor precision due to the various and multiple inoculums sources. Because of these reasons, it is very difficult to use in the petroleum laboratories for assessing the biodegradability of lubricants.

There are many models of varying complexity in the field of biodegradation technology. These models were originally developed based on the fundamental microbiological theory and their specific applications. But, none of these models is actually fitted or represented for the ASTM D 5864 biodegradation test. For this reason, a simple bio-kinetic model for the ASTM D 5864 test is essentially needed to predict the biodegradability of lubricants within a short time and to better understand the biodegradation process of lubricants. This paper describes a development of Bio-kinetic model, the determination of half-life of lubricant and its correlation with actual biodegradation data obtained from ASTM D 5864 test. The utility of the model presented here is not only for approximate biodegradation predictions, but also to provide information how it can

Report Documentation Page						*Form Approved OMB No. 0704-0188*
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.						
1. REPORT DATE **30 JUL 2004**		2. REPORT TYPE **N/A**				3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Development of Bio-Kinetic Model for Lubricants**						5a. CONTRACT NUMBER
						5b. GRANT NUMBER
						5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Rhee, In-Sik**						5d. PROJECT NUMBER
						5e. TASK NUMBER
						5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US Army RDECOM-TARDEC 6501 E 11 Mile Rd Warren, MI 48397-5000**						8. PERFORMING ORGANIZATION REPORT NUMBER **14190**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)						10. SPONSOR/MONITOR’S ACRONYM(S) **TACOM/TARDEC**
						11. SPONSOR/MONITOR’S REPORT NUMBER(S) **14190**
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release, distribution unlimited**						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT						
15. SUBJECT TERMS						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**SAR**	**10**		

improve biodegradability of lubricants.

BIO-KINETIC MODEL FOR LUBRICANTS

Development of General Bio-kinetic Equation:

The general rate equation for biomass growth and Monod equation are commonly used to model the kinetic of biodegradation or organic compounds and associated biomass growth[5]. The growth rate of biomass (Eq. (1)) is described by specific growth rate, μ and the concentration of biomass, X. This specific growth rate can be often determined using the Monod equation (Eq. (2)). It is described by the maximum specific growth rate, μ_m, concentration of substrate in solution, S, and the half-velocity constant (i.e., substrate concentration at which the specific growth rate is one-half of μ_m), Ks. From Eq (1) and (2), the degradation rate equation of the substrate (Eq. (3)) can express in terms of concentration of substrate and biomass in solution using a ratio of the increase in cellular mass to the decrease in mass of substrate, Y=dX/dt/dS/dt. This rate equation is widely used in biodegradation research and bioremediation.

$$\frac{dX}{dt} = \mu X \qquad (1)$$

$$\mu = \mu_{\max} \frac{S}{K_s + S} \qquad (2)$$

$$\frac{dS}{dt} = -\mu_{\max} \frac{SX}{Y\,(Ks + S)} \qquad (3)$$

However, this degradation equation requires the concentrations of biomass, S, maximum specific growth rate, and its half-velocity constant, Ks. These values are very difficultly obtained from the laboratory biodegradation tests. To simplify this equation, several mathematical expressions were attempted for describing the rate of biotransformation, including first- and zero-order approximations to the Monod model[6]. Of these expressions, the zero-order approximation was more appropriate in the laboratory biodegradation test with small amount of substrate. To introduce the zero-order approximation, the following two assumptions were made for this study.

(1) Substrate concentration (S) is much larger than its half-velocity constant, Ks.
(2) Weight of biomass (X) does not change much over time, X=Xo.

The term $(\mu_{max} X_o)/Y$ can be replaced by the term k which is referred to as the degradation rate constant. This results in the following expression for the zero-order approximation to Monod model:

$$\frac{dS}{dt} = -k \qquad (4)$$

This approximation is expressed in terms of only the rate constant instead of concentration of microorganism and substrate. To convert the concentration of substrate in Eq. (4) to the biodegradability (fractional conversion) of substrate, the following two terms are substituted in Eq. (4): $S=S_o(1-B)$, $-dS = S_o dB$. The biodegradation rate is expressed in terms of zero-order degradation rate constant, k and initial concentration of substrate. These constants denote as $K_b = k/S_o$. It was found that zero-order approximation of bio-kinetic model closely fit the actual data on a semi-log plot. Therefore, rearranging and intergrating for Eq. (4) gives a general form of Bio-kinetic model as below:

$$B(t) = B(1) + K_b \ln(t) \qquad (5)$$

where K_b: Biodegradation rate constant
$B(1) = 0.01$

Eq. (5) is expressed as a cumulative biodegradability of substrate for elapsed time t. B (1) was found to close to the first day of biodegradation which can be determined experimentally. The Bio-kinetic coefficient K_b can also be calculated from successive pairs of experiments or by the quarter life of substrate that was calculated using the composition analysis technique. This theoretical bio-kinetic equation generally agrees with an empirical equation that was found to be best fit the curve for biodegradation data obtained from the biodegradation tests. Figure 1 demonstrates the typical Bio-kinetic model with the actual biodegradation curve.

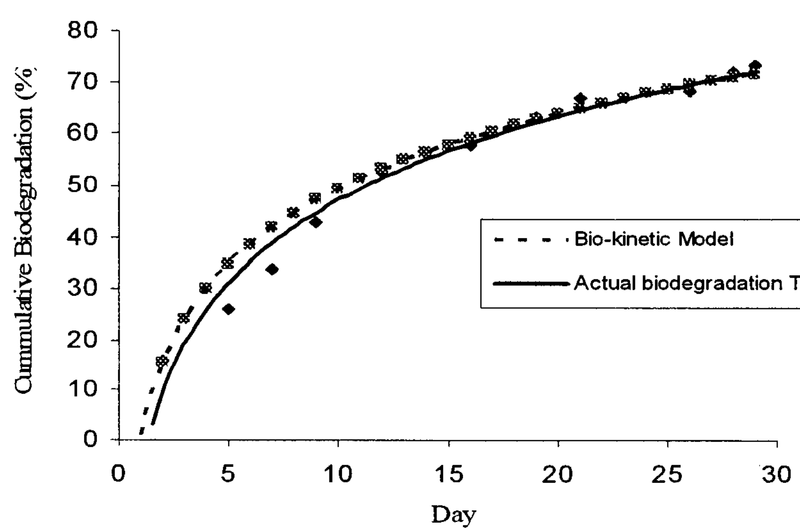


Figure 1. The Typical Bio-kinetic Model with the Actual Biodegradation Curve for BHF (MIL-PRF-32073)

Determination of Biodegradation Rate Constant, K_b using Half-life Theory and Composition Analysis:

The half-life of substrate, $t_{½}$ is defined as the time needed for the amount of substrate to drop to one-half of the original value. This approach has been used in kinetic modeling systems to predict the reaction order and the degradation rate of substrate[7, 8]. Currently, the half-life of lubricant is often measured directly from the actual biodegradation test. In this case, it still needs the biodegradation test apparatus and takes a long time to determine its biodegradation rate under a specified condition. For this reason, this approach does not apply for predicting the half-life of lubricant in a normal petroleum laboratory. It is desired to have a new methodology that can be used to predict the half-life value within a short period.

The inherent biodegradability of a lubricant depends to a large extent upon its molecular structure and material[9]. Typically, straight-chain aliphatic compounds (i.e., alkanes, cycloalkanes) are easily degraded. Simple aromatic compounds are usually slowly degradable and contain toxicity. Polymetric materials are among the most resist to microbial attack. It is also known that oils derived from renewable resources are more biodegradable than petroleum based oils. In addition, the water solubility or dispersability of petroleum based products, their molecular sizes, pH of solution, types of materials, temperature, total dissolved solids, and their toxicity, affect their biodegradability. Among them, it is strongly believed that the molecular structure and low toxicity may play a major role of biodegradation of lubricant products.

To better understand their inference to the biodegradation of lubricant products, a composition analysis was conducted using the ASTM D 2549, Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatogrphy. The schematic diagram of this test apparatus is shown in Figure 2. The test method tends to provide information on the separation and determination of representative aromatics and non-aromatics fractions from the petroleum based hydrocarbon oils using a chromatographic column. In a trial test, it was found that this procedure was not applicable to renewable based oils due to their inseparability problem. For this reason, some modification was made to analyze renewable products and its changes are listed in Table 1. Mainly, the modified procedure has a four-step process instead of a three-step process. The first step eluted non-aromatic materials using a pentane solvent. Then, non-polar based aromatics were eluted using a mixture of 50 % pentane and 50 % toluene instead of diethyl ether. In step 3 process, the esters or related products were eluted using a diethyl ether. The polar-based aromatics were eluted in the step 4 process.

Table 1. Modified ASTM D 2549 Procedure

Process	ASTM D 2549		Modified ASTM D 2549	
Step 1	Pentane	Non-aromatics	Pentane	Non-aromatics (saturate, mineral oil, PAO)

Step 2	Diethyl ether	Aromatics	50 % pentane+50% toluene	Non-polar based aromatics
Step 3	Chloroform/ethyl alcohol	Polar based Aromatics	Diethyl ether	Esters, acid, waxes
Step 4	-	-	Chloroform/Ethyl alcohol	Polar based Aromatics

The modified procedure was designed based on the diectricity of solvents and their eluting characteristics. It was fully evaluated using known samples prior to the tests. The major advantage of this test is its small sample size requirement (2g), and its good test precision. Because this procedure was originally developed for the liquid products, the grease can not be tested in this procedure due to its semi-solid form, but its base oil can be tested. As a matter of fact, the base oil of grease is the major contributor to the grease biodegradation than its thickener system. Also, it was found that this procedure can not differentiate some chemicals that eluted by same solvent such as mineral oil and PAO oils, or esters. In this case, the identification of oils can be directly obtained from oil manufacturers or through additional tests (i.e., Gas Chromatography (GC) or Infrared Spectroscopy (IR)).

Generally, the biodegradability of hydrocarbon based oils depends on the types of materials and chemical structures. For this reason, an adjustment was essentially needed for this composition analysis to determine the effective composition for the biodegradation (ECB) of lubricant. Table 2 lists the ECB coefficient for each type of oil. These coefficients were calculated based on the data obtained from biodegradation tests and range from 1 for the renewable ester to 0.01 for the Petroleum based ester type.

Table 2. ECB Coefficients for Oils

Lubricant	ECB Coefficient (η)
Mineral oil	0.3
PAO 2	0.8
PAO 4	0.6
PAO 6 or above	0.4
Natural esters	1
Renewable based diester	0.8
Petroleum based ester types	0.01

With these coefficients, ECB was determined using the equation (6). In this calculation, ECB is sum of all fraction of saturate and esters except for all aromatic fractions that are considered as toxic materials. In fact, the aromatics do not significantly contribute to the biodegradability of oil. The ECB of these samples were listed with their half-life in Table 2. In this study, the fifteen lubricants were selected from various applications. They consisted of three greases including a NLGI Non-EP reference grease (Batch 10), three biodegradable hydraulic fluids (BHFs, MIL-PRF-32073)[10], a mineral based base oil, a mineral based engine oil (MIL-PRF-2104)[11] and gear oil

(MIL-PRF-2105)[12], a petroleum based triester, a renewable based diester, and a fire resistant hydraulic fluid (MIL-PRF-46170)[13]. In addition, three different types of viscosity grades Polyalpaolefin (PAO) oils (2, 4, and 6 cSt) were also selected to clarify their biodegradability in the ASTM D 5864. A canola oil (cooking oil) was used as a reference sample for this test.

$$ECB = \sum_{i}^{j} (\eta_i C_i + \eta_j C_j) \tag{6}$$

where:
η : ECB coefficient
C_i: fraction of composition in Step 1
C_j: Fraction of composition in Step 3

To determine a biodegradation rate constant K_b, a correlation study was conducted between half-life and ECB of tested samples. It was found that the half-life of tested samples had a good correlation with their ECB. Figure 4 shows their correlation curve and correlation coefficient (r^2) that was found to be 0.98. Therefore, the half-life of lubricants, $t_{1/2}$, can be calculated using the following equation that was developed based on ECB:

$$\text{Half-life } (t_{1/2}) = 6.8 \times ECB^{-2.38} \tag{7}$$

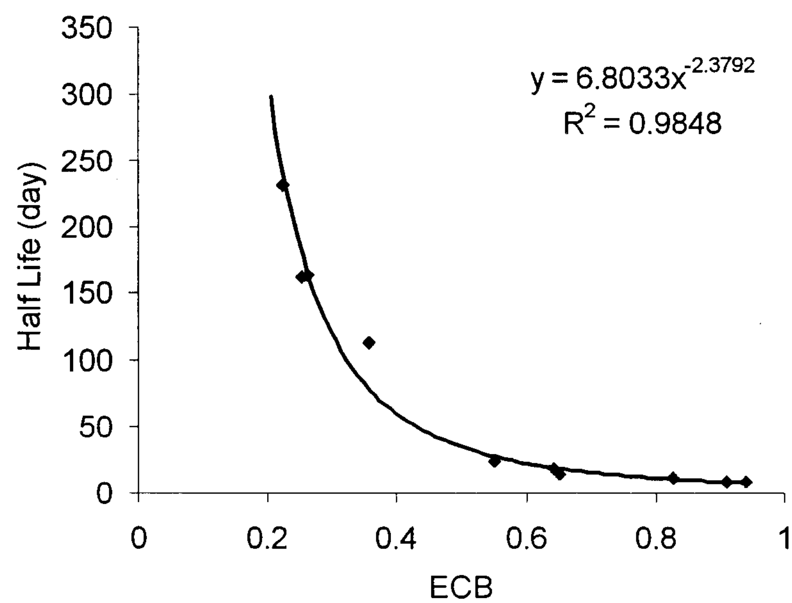


Figure 4. Correlation between ECB and Half Life

Based on the equations (5) and (7), a practical equation (8) was developed for calculating the biodegradation rate constant, K_b from their half –life. The number 0.49 is simply the difference from the 50 % biodegradation to 1 % of biodegradation found after the first day.

$$K_b = 0.49/\ln(\text{Half-life}) \qquad (8)$$

The above equation can significantly contribute to find the K_b value that is a very important parameter of the Bio-kinetic model. This calculated K_b value gave a very good agreement with that obtained from the biodegradation test.

Table 2. Composition Analysis and Half-life of Tested Lubricants

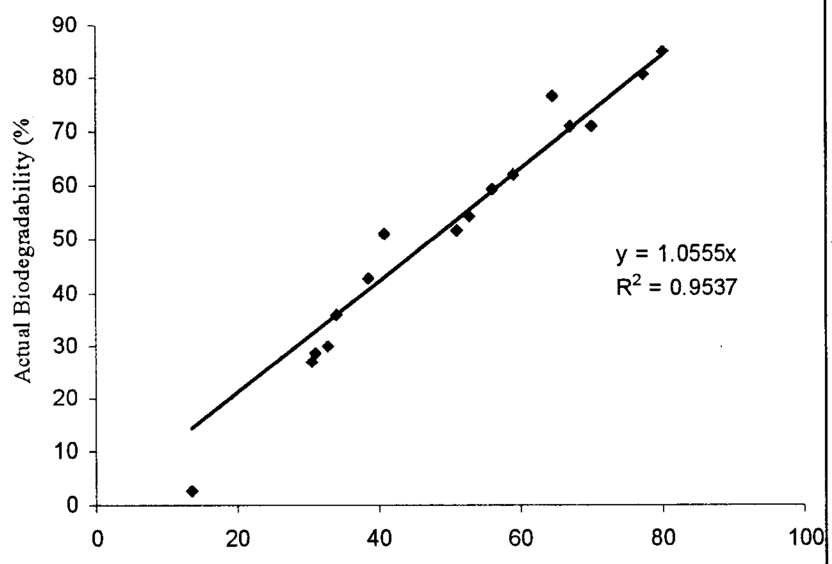
Code	Lubricants	Types of oils	Alkanes or Saturates	Non-polar Aromatics	Ester, Acid or Wax	Polar material	ECB	Half-life
A	NLGI Non-EP grease (Batch 10)	Mineral	73.4	25.1	0.4	1.2	0.224	231
B	Engine oil	Mineral	82.5	13.5	1.4	1.7	0.262	164
C	Military Automotive Grease	PAO 6 and Mineral	92.9	2.63	1.69	2.8	0.252	162
D	Gear oil	Mineral	73.0	10.6	13.7	2.7	0.356	114
E	FRH	PAO 4 and Ester	68.7	2.9	27.7	0.7	0.55	25
F	BHF A	PAO 4 and Ester	53.4	0.28	42.9	3.5	0.643	18.8
G	BLG	PAO 4 and Ester	44.0	2.6	47.6	5.9	0.652	14.6
H	BHF B	Ester +Mineral	17.5	1.32	77.5	3.7	0.828	12.1
I	BHF C	Ester	0.6	2.2	93.5	5.1	0.94	5.5
J	Base oil A	PAO 2	98.8	0.47	0.05	0.7	0.79	11.9
K	Base oil B	PAO 4	99.0	0.21	0.09	0.7	0.59	23.4
L	Base oil C	PAO 6	99.0	0.07	0.1	0.8	0.4	61.3
M	Base oil D	Triester	0.05	0.44	96.8	2.7	0.01	ND
N	Base oil E	Diester	0.04	3.14	95.0	1.8	0.76	14.8
O	Base oil F	Mineral	93.7	5.5	0.11	0.49	0.28	ND
P	Canola (cooking oil)	Ester	0.18	1.6	90.7	7.5	0.91	9.1

CORRELATION BETWEEN ASTM D 5864 BIODEGRADATION TEST AND BIO-KINETIC MODEL

To validate the Bio-kinetic Model, several laboratory biodegradation tests were conducted using the ASTM D5864 test apparatus. This test method was originally designed to determine the degree of aerobic aquatic biodegradation of lubricant products on exposure to an inoculum under laboratory conditions. In this test, the biodegradability of lubricant products is expressed as the percentage maximum (theoretical) carbon conversion (or carbon dioxide generation) under well-controlled conditions for a period of 28 days. A schematic diagram of the ASTM D 5864 biodegradation test apparatus is shown in Figure 3. This test apparatus was a slightly modified for the study. It consists of four separate units: the air supply/carbon-dioxide scrubbing system, the incubation/biodegradation batch reactor, a carbon-dioxide collector, and a titrator. Both the carbon-dioxide scrubbing and the biodegradation units utilize Erlenmeyer flasks. To eliminate other carbon sources, except the test lubricant, CO_2-free air is needed for the biodegradation test. A laboratory compressed air supply was attached directly to the carbon dioxide scrubbing system to produce CO_2-free air. The scrubbing system uses cascade flasks: two flasks containing 10M potassium hydroxide (KOH) solution and two flasks containing 0.025M barium hydroxide Ba $(OH)_2$ solution. To ensure the desired aerobic environment, the test solution containing the test lubricant was fully agitated using a variable speed magnetic stirrer. In order to conduct multiple tests for performance comparison, ten separated identical biodegradation batch reactors were connected as seen in Figure 2. Each reactor can be independently and flexibly operated for aquatic biodegradation tests.

To measure carbon dioxide production during a predetermined test period, the CO_2 collector nearest the 4 L Erlenmeyer flask was removed for titration and calculations. The remaining two collectors were moved up one place closer to the 4 L Erlenmeyer flask and a new collector filled with 100 mL of fresh 0.0125 M Ba $(OH)_2$ was placed at the far end of the series. Titration was performed every day for the first 10 days and then every other day for the remaining 18 days or until a plateau of CO_2 evolution was reached. The end point used for automatic titration was set at pH 7. Once the CO_2 evolution has reached a plateau, the pH of the test solutions were measured and added 1 mL of HCL into the test solutions to decompose the inorganic carbonate and to release trapped CO_2 for a final titration. Data obtained from the titration were converted to the amount of CO_2 production using an equation specified by the method.

For a correlation study, fifteen lubricant products listed in Table 2 have been tested according to the ASTM D5864 biodegradation test method and their biodegradability were determined after 28 days. A summary of the biodegradation test results is presented with their predicted biodegradability calculated from Bio-kinetic model in Table 4. It is noted that these results were determined based on duplicate test results in order to increase reliability of test data. In this biodegradation test, the natural ester based lubricants gave a very good biodegradability, while a petroleum-based ester had very low biodegradability. PAO 2 cSt oil also gave a good biodegradability among other PAO grades. As expected, the NLGI non-EP grease marked a low biodegradability due to its base oil. These test results clearly indicated that the biodegradability of lubricants significantly depends on their base oil material and chemical structures. To determine a correlation coefficient (r^2) between actual biodegradation data and bio-kinetic model, the data were analyzed using a statistic method and plotted in Figure 5. Its correlation coefficient (r^2) was found to be 0.95. This value can be acceptable for the study. It appears that the Bio-kinetic model developed is able to predict the biodegradability of lubricants without the ASTM D 5864 biodegradation test. This Bio-kinetic model only requires the ECB of lubricants obtained from the modified ASTM D 2549 composition analysis method. Therefore, this Bio-kinetic model can be used to predict the biodegradability of lubricants within a very short period.



Fgure 5. Correlation between Actual vs. Predicted Biodegradability

CONCLUSIONS

On the basis of the work completed to date, a Bio-kinetic Model for lubricants was developed for the ASTM D 5864 biodegradation test. The results of this study are summarized in the following findings:

1. Bio-kinetic model gave a good agreement with the results of ASTM D 5864 biodegradation test. Their correlation coefficient (r^2) was found to be 0.95.
2. Modified ASTM D 2548 test method is able to analyze the composition of lubricants. But, it can not differentiate between mineral oils and PAO oils and between renewable

ester and non-renewable ester. It requires pre-information of base oil composition from oil manufacturers or other techniques (i.e., IR, GC).
3. The effective composition for biodegradation (ECB) gave a good correlation with the actual half-life of lubricant obtained from ASTM D 5864 biodegradation test.
4. ECB can provide vital information on how to improve the biodegradability of lubricants.
5. The biodegradation rate constant (K_b) can be calculated using a half-life of the lubricant.
6. Bio-kinetic model can be used to predict the biodegradability of lubricants within a very short period.

ACKNOWLEDGEMENTS

This study was conducted as a part of U.S. Army In-house Laboratory Independent Research (ILIR) Program. The assistance of Lori Zuziak and Rachel Jackman who conducted most of biodegradation tests is gratefully acknowledged. The author also whishes to thank Mr. Ronald Krol of Summit Lubricants Company, Mr. Gene Zehler of Cognis Company, and Mr. John Harris of Shell Oil Company for providing oil samples and their contribution of this study.

REFERENCES

1. .P. Flathman and D. Jegrer, "Bioremediation-field Experience", CRC Press, Inc., pp. 429-456, 1994.
2. Tortora, Funks, and Case, Microbiology, Fifth Edition, The Benjamin/CummingsPublishing Company, New York, NY. pp.14-17, 1995.
3. Donna Hole, "Lubricants and Environment", ASTM Stantardization News, pp. 41-45, June 1995.
4. In-Sik Rhee, "21th Century Military Biodegradable Greases", NLGI Spokesman Vol. 64, No.1, April, 2000.
5. Michael L. Shuler, Bioprocess Engineering, Prentice-hall, Inc., pp. 148-198, 1997.
6. Barbara A. Bekins, Ean Warren, and E. Michael Godsy, "Comparing Zero- and First Order Approximations to the Monod Model", In-Site and On-Site bioremediation: Volume 5, Batell Press, pp. 547-552.
7. Octave Levenspiel, Chemical Reaction Engineering, Second Edition, John Wiley and Sons, Inc., pp-41-54, 1972.
8. Michasel D. LaGrea, Hazardous Waste Management, McGraw Hill, Inc., pp. 572-583, 1994.
9. John Cookson Jr., Bioremediation Engineering, McGraw-Hill, Inc., pp. 359-429, 1995.
10. Military Specification, MIL-PRF-32073, Hydraulic Fluid, Biodegradable, 2001.
11. Military Specification, MIL-PRF-2104, Lubricating Oil, Internal Combustion Engine, \ Combat/Tactical Service, 2004
12. Military Specification, MIL-PRF-2105, Lubricating Oil, Gear, Multipurpose, 1995
13. Military Specification, MIL-PRF-46170, Hydraulic Fluid, Rust Inhibited, Fire Resistant Synthetic Hydrocarbon Base, 2001.